STUDIES IN COLORIMETRIC AND VOLUMETRIC IODIMETRY

by

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A THESIS

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INTRODUCTION

The titration of iodine with sodium thiosulfate using starch as an indicator, may be considered as one of the most accurate and convenient processes in analytical chemistry. The starch indicator, with even a minute excess of free iodine, gives a deep blue complex of known composition.

The study of starch properties and its usages has long held the interest of many research workers. It is known that starch is widely distributed in the vegetable kingdom and it is one of the largest sources of cheap organic chemicals. A large portion of the starch that is produced is converted to syrups and dextrose, mainly for food, but there are numerous applications in the industrial fields such as pastes, plastics, films, and chemical reagents with the ultimate use being determined by their measured properties.

Starch granules, when viewed under the microscope, differ considerably in size but they are characteristic of the plants from which they come. For example, granules of potato starch are quite coarse whereas those of rice are very fine. Nevertheless, all types of starch give a blue color with iodine, and this coloration is the basis of a test for starch or conversely, for iodine. Such a test can be used to follow the progressive stages of starch hydrolysis in which the color of the starch iodide complex changes from blue to faint red and finally becomes colorless. It is used also as an end point indicator in methods for iodine determinations.

Starch granules are composed of two similar but distinct substances, amylopectin and amylose. The amylose corresponds roughly to the linear starch A fraction and is held within the envelope of the granule which is composed of amylopectin. When starch is stirred in hot water, this process causes the granule to swell and burst, thus releasing the amylose to form a colloidal suspension in water. Schoch (23,24) has successfully found a method

by which amylose could be crystallized from aqueous solution saturated with 1-butanol. This crystallized product has been shown to possess a high degree of homogenity.

In analytical work, several factors led to an early utilization of iodine methods. A sensitive starch indicator has been long known, and a reagent, sodium thiosulfate, was available for quantitative titration of iodine. Because of these conditions, a large number of analytical methods have been developed about the iodine-iodide-ion equilibrium. However, starch indicator as it was used in earlier work was not stable since homogeneous and reproducible starch was not available and the starch solution over a period of time deteriorated due to the action of bacteria. The literature mentioned numerous methods where chemical preservatives were used to prolong the sensitivity of starch solutions.

Brooks (3) noticed that a starch solution containing 10 grams of starch per 500 ml. to which there had been 5 grams of sodium hydroxide did not deteriorate or lose its sensitivity over a period of four months.

Painter (17) boiled common household rice starch and an equal weight of sodium carbonate with water. After cooling the solution, he added concentrated hydrochloric acid until the solution was acid. After the addition of little zinc, the solution was set aside for 24 hours and then filtered. Tests showed that the solution was still a good indicator after eight months.

Minovici (13) indicated that the starch solution was stabilized by the addition of 0.1 gram mercuric chloride per 250 ml. solution containing 0.5 gram starch.

Nichols (16) discovered that the addition of salicylic acid stabilized the starch solution.

Lambert et al. (9) found that cadmium iodide not only stabilized the

starch solution but also showed the results in its use were reproducible. According to Lambert et al. the stability of the solution is due to the formation of cadmium iodide complexes and the natural toxicity of cadmium. The starch used in the solution was homogeneous linear starch prepared by Schoch method. Throughout the investigation, this reagent, cadmium iodide-linear starch, was used.

The nature of the interaction between the starch and the iodine to form the blue color has aroused the interest of chemists since 1812. Explanation should be made that it is not the pure iodine which gives the bright blue color but the triiodide, I_3^-, ion.

The first report of the starch iodine reaction was made by Colin and Gaultier de Claubry (4) who studied the effects of various classes of organic substances on iodine. The most remarkable of these effects were with starch. From that time until the present, numerous views, each differing from the others, of the starch iodine reaction have been expressed.

Personne (18) regarded starch iodide as a lake. Duclaux (5) considered it to be a case of molecular adhesion and that its formation was dependent on the equilibrium between the starch, iodine and water.

Mylius (15) assigned the formula, $\left[(C_6H_{10}O_5)_nI\right]_4$,HI and later $(C_{24}H_{40}O_{20}I)_4$, for starch iodide. He discovered that hydrochloric acid or an iodide entered into the composition of the blue starch compound and that the "starch iodide" was not simply starch plus iodine as indicated by others.

Küster (8) was concerned mainly with the composition of the precipitate produced in a starch solution in which iodine in potassium iodide and dilute sulfuric acid were added. He concluded from his experiments that the blue starch iodide was a solution of iodine in starch.

A number of authors investigated the partition of iodine between starch and organic solvents such as carbon tetrachloride, chloroform, benzene, toluene and s-tetrachloroethane. Most of these investigations (1,6,11,14,27,28,29) led to the conclusion that starch iodide has no definite composition, and that it is an adsorption compound.

Bergmann (2) pointed out that the problem is not necessarily one of adsorption of chemical union, but that both kinds of combination may well occur together. He postulated that a chemical compound with a fixed proportion of iodine may well adsorb more iodine in varying amounts and in such cases the iodine is comparable to water of hydration.

Rundle and his co-workers (20,21,22) presented the best evidence. They found through X-ray diffraction, optical, potentiometric and spectrophotometric analyses that the starch iodide complex is definitely a compound formation and that the structure of the complex to be helical amylose chain with the iodine molecules arranged inside, parallel to the helix. Each turn of the amylose helix contained six glucose units and only the amylose formed the bright blue color which was dependent on the chain length.

Much of the work seems to be conflicting. Such disagreements could be due to many variables operating during the experiments. However, the explanations could be classified into two general catagories: (1) the adsorption of iodine or solid solution formation, (2) the formation of a new "compound."

One logical approach is to utilize the starch iodide complex in colorimetric analyses. This study has been made to investigate whether this technique could be used in determining chloride ions quantitatively. As a method of attack, an ion exchange column was set up with the column material being of such a nature that would exchange for chloride ions readily. Silver iodate, being practically insoluble in water solution, possessed such a property.

The chloride ions exchanged for iodate ions from granular silver iodate. The concentration of chloride ion was determined by the absorbance of the blue linear starch-triiodide ion complex formed by the reaction of the released iodate ion with cadmium iodide-linear starch reagent in acid solution.

One aspect related to this colorimetric method was the preparation and characterization of a primary reducing agent, anhydrous trisodium monothiophosphate, which is very similar to the sodium thiosulfate which has been used heretofore. Preliminary work involved a method where the sodium salt could be obtained in good yield as well as a solvent that would purify it by removing all by-products formed during the reaction. Wurtz reaction (12),

$$PSCl_3 + 6NaOH \longrightarrow Na_3PO_3S + 3NaCl + 3H_2O$$

proved to be advantageous. Other methods of preparation either failed or proved to be tedious. The sodium salt obtained through Wurtz method contained sodium chloride as a contaminant but treatment with absolute methanol dissolved it and also dehydrated the trisodium monothiophosphate.

The present work was undertaken to find an accurate and rapid colorimetric method using the starch iodide complex as a means of determining chloride ion quantitatively in natural waters between the range of 0-180 p.p.m. As a secondary problem, investigation of anhydrous trisodium monothiophosphate as a potential primary reducing agent for iodine methods was evaluated.

EXPERIMENTAL PROCEDURE A (10)

Preparation of Granular Silver Iodate

Pure silver iodate may be purchased, but it was prepared by reacting 0.1 mole each of silver nitrate and potassium iodate in dilute solution. It was prepared under nearly homogeneous conditions by dissolving each salt in 500 ml. of distilled water and allowing both solutions to drip slowly at the same rate into a liter of rapidly stirred water. After precipitation was complete, the product was washed and dried. Small batches were carefully melted and poured into cold water, forming hard masses which were ground and sieved to the desired 100-200 mesh size. Silver iodate decomposed slightly on melting, but the resulting silver iodide did not affect the reactions of the granular silver iodate. The pure salt was white, but turned yellowish-white on melting due to the silver iodide formed.

Preparation of Silver Iodate Column

The column was prepared by firmly tamping a small plug of borosilicate glass wool into the buret constriction above the stopcock. The buret was filled half full with water and a slurry of the granular silver iodate was poured in to form a column 6 cm. high. A second borosilicate glass wool plug was packed on top of the column to keep the silver iodate particles firmly in place. The column was never allowed to run dry, and distilled water was kept in the buret at all times when the column was not in use.

Preparation of Pressure Bulb Assembly

The pressure bulb was very convenient for forcing wash water through the column. A short length of flexible tubing was attached to a double acting

rubber bulb in such a manner that the bulb acted as a source of air pressure. A No. 00 one-hole rubber stopper, which fitted the top of the buret, was attached to the other end of the rubber tube by means of a short length of glass tubing. Whenever the column was accidently allowed to run dry, it could be reverse-flushed by reversing the rubber bulb and using it to suck distilled water up through the column.

Procedure of Analysis

The column in the buret was washed twice with the solution to be analyzed by filling the buret with the stopcock closed and inverting to empty the solution. The closed stopcock prevented the liquid around the silver iodate particles from being drained out. The glass wool plug on the top of the column effectively prevented the liquid from draining out of the column if the rinsing solution was poured off quickly. A buret full of the solution was allowed to run through at normal speed (about 80 drops per minute), or alternatively, two burets full were forced through by the use of the pressure bulb.

The buret was filled approximately to the zero mark, and the solution was allowed to run through until the meniscus was exactly on the 10 ml. mark. The next 10 ml. were very carefully measured into the 100 ml. volumetric flask and diluted up to the calibration mark with distilled water. After thoroughly mixing, 10 ml. of this solution were pipetted into a 250 ml. volumetric flask, and diluted up to the calibrated mark. From this, 20 ml. were taken as a sample and 1.0 ml. each of 1.0 N hydrochloric acid and cadmium iodide-linear starch reagent were added. The absorbance of the solution at 615 mμ was determined five minutes from the time the acid and the starch iodide reagent were added. The absorbancies produced at all the concentrations studied were practically constant between five and twenty minutes after the addition of the acid and starch reagent.

Other Reagents and Equipment Used

Cadmium iodide-linear starch reagent, 11.0 grams of cadmium iodide and 2.50 grams of twice recrystallized linear potato starch fraction per liter of solution (Lambert, et al., 9).

Standard chloride ion solution, 200 p.p.m., 0.330 gram of sodium chloride per liter of solution.

Spectrophotometer, Beckman Model DU, 10 mm. cells.

Chemical Analyses

Chloride Determination. Mohr's method (Pierce and Haenisch, 19) was used as a standard method in checking the results obtained from water analyses by this new colorimetric method. The results include actual analyses of natural waters and the addition of known amounts of standard chloride solution. These data are summerized in Table 2.

EXPERIMENTAL PROCEDURE B (30)

Preparation of Thiophosphoryl Chloride

The method of Knotz (7) was found to be most convenient for preparing thiophosphoryl chloride on laboratory scale. Phosphorous trichloride (54.6 ml.) and powdered sulfur (20.1 g.), with anhydrous aluminum chloride (approximately 2 g.) added as catalyst, were reacted under reflux. The reaction was often vigorous, although slight heating was necessary to initiate it. The reaction products were distilled and the fraction boiling between 120-125°C was collected.

Preparation of Anhydrous Thisodium Monothiophosphate

Sodium hydroxide (40.0 g.) in 300 ml. of aqueous solution was heated with thiophosphoryl chloride (17.5 ml.) under reflux at 110-115°C for fifteen minutes or more, until the thiophosphoryl chloride layer disappeared. The solid trisodium monothiophosphate and sodium chloride salts crystallized out on cooling in an ice bath. These were filtered off and dissolved in a minimum quantity of warm (40-45°C) water. For each 100 ml. of salt solution, approximately 185 ml. of anhydrous methanol was added to precipitate the trisodium monothiophosphate hydrated salt. This recrystallization procedure was repeated and the hydrated salt dehydrated by suspending it, with constant stirring for one hour, in 200 ml. of anhydrous methanol. The white anhydrous trisodium monothiophosphate crystals were filtered with suction at room temperature, heated at 100°C for one hour and stored in a tightly stoppered bottle.

Chemical Analyses

Sulfur Content. The sulfur content was determined by standard gravimetric method (Pierce and Haenisch, 19) where the sulfur was oxidized to sulfate and weighed as barium sulfate. The calculated values and those found experimentally are listed in Table 3.

Phosphorous Content. The phosphorous was oxidized to the phosphate using a standard gravimetric method (Pierce and Haenisch, 19) and weighed as magnesium ammonium phosphate. The results are listed with the calculated values for comparison in Table 4.

Purity of Trisodium Monothiophosphate. Titration with standard iodine solution in the pH range of 0.5-0.8 using potentiometric end point with polarized platinum wire electrodes was used assuming the reaction (Thio and Schone, 26):

$$2(PO_3S)^{\equiv} + 2H^+ + I_2 \rightleftharpoons (HO_3PSSPO_3H)^{=} + 2I^-$$

to be true. The results thus found are given in Table 5.

EXPERIMENTAL RESULTS A

From the data given in the literature (Seidell, 25), the solubility product constant of silver iodate at 25°C was calculated to be 3.57×10^{-8}, and that of silver chloride to be 1.85×10^{-10} at the same temperature. At equilibrium, the ratio of iodate ions to chloride ions in solution would be 193. Equilibrium was apparently reached quickly in the column, as the dark band of silver chloride was seen to form at the very top of the column and progress downward slowly as long use of the column exhausted the silver iodate. Less than one-fourth of an inch of the column was darkened as a result of all the determinations made in this study, indicating a long useful life for the column. Silver iodate is not very light sensitive but should be protected from direct light by using an opaque shield around the silver iodate area of the buret.

The calibration curve, (Fig. I), was determined using pure sodium chloride solutions of known concentrations. The vertical diameter of each circle indicated the range of four determinations made at that concentration. The relationship apparently would be linear over a greater range than is shown, but practical difficulties in reading the absorbancies in high concentrations limited the concentrations that could be determined directly. The loss of precision at higher concentrations could be due partly to errors in reading absorbance values. The optimum concentration range for analysis without resort to dilution was apparently 0-150 p.p.m. chloride ion.

A faintly colored blank was obtained when distilled water was run through the column and determined in the regular manner. This could perhaps

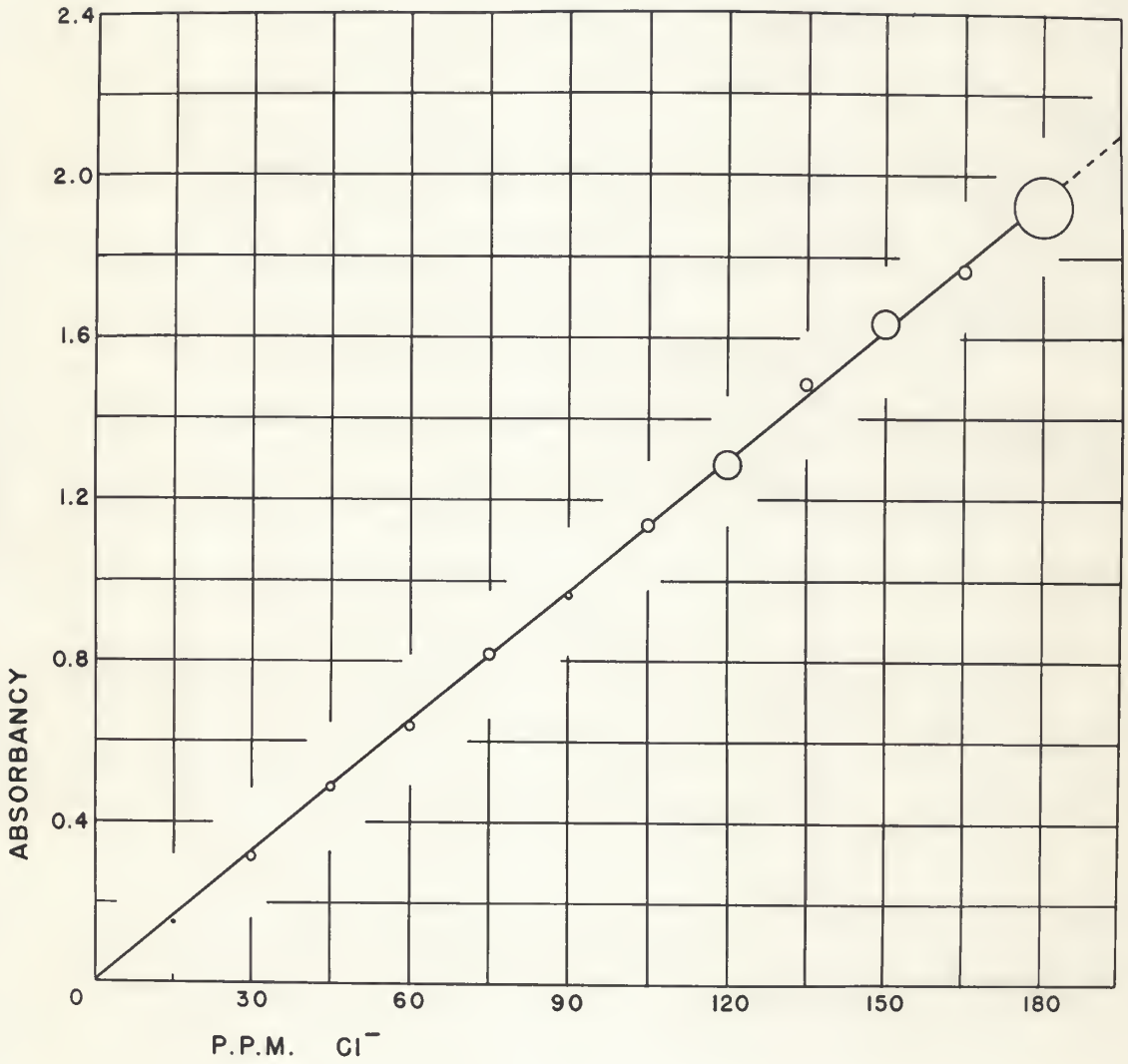

Fig. 1. Calibration Curve

be reduced by greater dilution, but at a loss of sensitivity of this method. Owing to the slight solubility of silver iodate, the absorbance of the blank was very small but constant. The solutions analyzed in Fig. I were compared to such blanks obtained at the time each series of samples were determined. Another calibration curve was obtained by comparing the absorbancies against distilled water as a reference. This line was displaced upwards at all concentrations by the optical density of the zero chloride ion blank. The constant value of this blank would justify the use of distilled water as a reference in spectrophotometric determinations. No attempt was made to control temperature for any of the determinations.

Potential interferences were studied up to a maximum of 500 p.p.m., with the results shown in Table 1. The colors produced by the various substances shown which were approximately the same as the zero chloride ion blank were listed as "equals blank", and are considered not to interfere. From this data, it is evident that very few ions would interfere at the concentrations usually found in natural waters or drinking water supplies. The inorganic salts of several of the cations showed interference at slightly lower concentrations than the acetate salts of the same cations. This was probably due to trace amounts of chloride ions present as an impurity in the inorganic salts. Bromide and iodide ions would give the same reactions as chloride ion but they are not usually present in natural waters in concentrations that would give high chloride ion values.

Chloride ion concentration in two representative waters were analyzed with the results shown in Table 2. Determinations were made on the raw samples and on samples to which known amounts of chloride ion were added. The river water, after the removal of suspended matter, was diluted with 200 p.p.m. standard chloride ion solution to give the desired increase in

chloride concentration. Solid sodium chloride was added to one batch of the city water to give the increased chloride ion concentrations. The values obtained by this method agree well with those obtained by the Mohr method.

Table 1. Effect of possible interferences.

Substance		Chloride Ion Absent Concentration, P.P.M.	Color
F^-	NaF	50	equals blank[a]
NO_3^-	KNO_3	500	equals blank
HCO_3^-	$NaHCO_3$	500	equals blank
$C_2H_3O_2^-$	$NaC_2H_3O_2$	500	equals blank
SO_4^{--}	$ZnSO_4$	500	equals blank
HPO_4^{--}	Na_2HPO_4	50	equals blank
K^+	$KC_2H_3O_2$	500	equals blank
Na^+	$NaC_2H_3O_2$	500	equals blank
NH_4^+	$NH_4C_2H_3O_2$	300	appreciable[b]
		200	equals blank
Ca^{++}	$Ca(C_2H_3O_2)_2$	400	equals blank
Mg^{++}	$Mg(C_2H_3O_2)_2$	300	appreciable
		200	equals blank
Zn^{++}	$Zn(C_2H_3O_2)_2$	500	equals blank
Al^{+++}	$Al(NO_3)_3$	300	equals blank
Fe^{+++}	$Fe(NO_3)_3$	300	appreciable
		200	equals blank
H^+	H_2SO_4	10^{-3}N	equals blank
OH^-	NaOH	10^{-3}N	equals blank

a. Color approximately as intense as that obtained with distilled water by the regular procedure.
b. Significantly more color than is produced by distilled water.

Table 2. Analysis of typical water samples

Sample	No. of Detns.[a]	Cl^- Added, P.P.M.	Cl^- Found, P.P.M.	
			Mohr Method	This Method
I[b]	5	0	68	
	4	0		70
	4	16		84
	4	32		100
II[c]	5	0	29	
	2	0		28
III[d]	4	0		28
	4	25		55
	4	50		79
	4	100		130

a. Good agreement between results of multiple determinations.
b. Kansas river water collected near Manhattan, Kansas, with suspended solids removed by filtration and/or centrifugation.
c. Manhattan, Kansas, city water supply, obtained from wells in the Blue River valley.
d. Manhattan, Kansas, city water supply, different date.

EXPERIMENTAL RESULTS B

It has been found that the anhydrous sodium monothiophosphate, Na_3PO_3S, was very stable at room temperature and could be heated at 100°C without decomposition. Between 120°-125°C, the anhydrous trisodium salt decomposed very slowly without melting to release a volatile compound which discolored lead acetate paper. Solubilities in grams per liter of saturated solution at various temperatures are: 4°C., 21.2; 18°C., 79.2; 28°C., 132.7; 38°C., 241.5. Solutions of the sodium salt decomposed slowly, but are apparently very stable when stabilized with sodium carbonate. A solution containing 10 per cent sodium carbonate proved to be relatively stable for several months.

The theoretical calculation for sulfur and phosphorous in trisodium monothiophosphate was found to be 17.83 per cent and 17.27 per cent respectively. Experimentally, the determined values were in good agreement as shown in Tables 3 and 4.

Table 3. Gravimetric analysis of sulfur.

Wt. of Na_3PO_3S	Weighed as $BaSO_4$	Calculated values % sulfur	Experimental values % sulfur
0.500 g.	0.6544 g.	17.83	17.97
"	0.6467	"	17.78
"	0.6515	"	17.90
"	0.6434	"	17.68

Table 4. Gravimetric analysis of phosphorous.

Wt. of Na_3PO_3S	Weighed as $MgNH_4PO_4 \cdot 6H_2O$	Calculated values % phosphorous	Experimental values % phosphorous
0.500 g.	0.6764 g.	17.27	17.09
"	0.6878	"	17.38
"	0.6434	"	17.25

To supplement this gravimetric analyses, titration with standard iodine solution in the pH range 0.5 to 0.8, using a potentiometric endpoint with polarized platinum wire electrodes, gave consistent results between 99.9 per cent to 100.0 per cent of calculated purity. The data obtained are shown in Table 5.

Table 5. Determination of purity by iodimetric titration.

Wt. Na_3PO_3S	Vol. 3·5N·HCl	Vol. H_2O	Vol. St'd. I_2	% Purity
0.2532 g.	7 ml.	100 ml.	13.55 ml.	99.85
0.2529	7	100	13.55	99.98
0.2498	7	100	13.45	100.00
0.2492	10	100	13.45	100.00
0.2518	10	100	13.55	99.95
0.2500	10	100	13.45	99.90

The anhydrous sodium salt showed remarkable reducing power and it may be considered to have properties similar to sodium thiosulfate. It decolorized potassium permanganate, iodine, reducing them to manganous and iodide ions respectively. As a qualitative test, salts of mono-, di-, and trivalent metals were prepared. These tests resulted in very unique qualitative determination for cobaltous ion in the presence of nickelous ion.

SUMMARY AND CONCLUSION

A very accurate and rapid method has been described by which chloride ion could be determined colorimetrically over the range 0-180 p.p.m. after exchanging for iodate ion with granular silver iodate in the column. The released iodate ion reacted with cadmium iodide-linear starch reagent in acid solution to form the blue linear starch-triiodide ion complex. The absorbance of the complex at 615 mμ was proportional to the concentration of chloride ion. The calibration curve prepared from standard chloride solutions of known concentrations adhered very closely to Beer's law. In actual analyses of natural waters, this method showed good agreement with the Mohr method. No serious interferences were found among ions commonly found in natural waters within the limits of their usual concentrations.

The anhydrous trisodium monothiophosphate which was not previously known has been prepared. This anhydrous salt has been found to be stable and nondeliquescent under ordinary conditions, whereas the commonly known hydrated salt is not stable.

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A faintly colored blank was obtained when distilled water was run through the column and determined in the regular manner. This could be reduced by greater dilution, but at a loss of sensitivity of this method. The absorbance of the blank was very small but constant and this was due to the slight solubility of silver iodate. The two calibration curves obtained by comparing the absorbances against distilled water and the faintly colored blank as references, were in both cases to be linear and displaced equidistant upward at all concentrations. The constant value of these blanks justified the use

of distilled water as a reference.

Potential interferences were studied up to a maximum of 500 p.p.m. Very few ions interfered at the concentrations usually found in natural waters. Analyses of chloride ion concentration in two representative waters were made on the raw samples and on samples to which known amounts of chloride ion were added. The values obtained by this method agreed well with those obtained by the Mohr method.

One aspect related to this colorimetric method was the evaluation of anhydrous trisodium monothiophosphate as a potential primary reducing agent for iodimetry. Wurtz reaction was used in preparing the hydrated sodium salt. Sodium hydroxide (40.0 g.) in 300 ml. of aqueous solution was heated with thiophosphoryl chloride (17.5 ml.) under reflux at 110-115°C. for fifteen minutes or more, until the thiophosphoryl chloride layer disappeared. The solid trisodium monothiophosphate and sodium chloride salts crystallized out on cooling in an ice water bath. These were filtered off and dissolved in a minimum quantity of warm water. For each 100 ml. of salt solution, approximately 185 ml. of anhydrous methanol was added to precipitate the trisodium monothiophosphate hydrated salt. This recrystallization procedure was repeated and the hydrated salt dehydrated by suspending with constant stirring for one hour in 200 ml. of anhydrous methanol. The white anhydrous trisodium monothiophosphate crystals were filtered with suction at room temperature, heated at 100°C. for one hour and stored in a tightly stoppered bottle.

It was found that the anhydrous trisodium monothiophosphate, Na_3PO_3S, was very stable at room temperature and could be heated at 100°C. without decomposition. The sodium salt was very soluble in water and this could apparently be stabilized with the addition of sodium carbonate. A solution

containing 10 per cent sodium carbonate proved to be relatively stable for several months.

The purity of anhydrous trisodium monothiophosphate was determined by gravimetric analyses of sulfur, phosphorous and iodimetric titration using potentiometric endpoint with polarized platinum wire electrodes. Results between 99.90 per cent to 100.0 per cent of calculated purity were obtained.

The anhydrous sodium salt showed remarkable reducing power and it may be considered to have similar properties as sodium thiosulfate. It decolorized potassium permanganate, iodine, reducing them to manganous and iodide ions respectively. As a qualitative test, salt of mono-, di-, and trivalent metals were prepared. This in turn resulted in a very unique qualitative test for cobaltous ion in the presence of nickelous ion.